Science of Sintering, **41** (2009) 143-150

doi: 10.2298/SOS0902143B

UDK 622.785:669-138

In-situ Processing of TiB_2 Nanoparticle-Reinforced Copper Matrix Composites

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Abstract:

In order to produce the composite powder analyzed in this paper, two prealloys were melted and afterwards gas atomized. The obtained TiB_2-reinforced copper powder was consolidated by hot isostatic pressing (HIP). Since it is known that a decrease in the size of the reinforcing phase can cause an increase in hardness of composites, the main aim of the experimental work was to obtain as small particles of the dispersed phase as possible by using standard powder metallurgy techniques. Microstructure and microhardness of the as-cast prealloys, as-atomized powder and HIP-ed compacts were examined. The results of these examinations revealed that TiB_2 particles about 10 nm in size were in-situ formed and homogenously dispersed in the copper matrix. As a consequence of the TiB_2 formation, the microhardness of Cu-TiB_2 composite was significantly improved.

Keywords*: Cu-TiB_2 composite; Powder metallurgy; Hot isostatic pressing; TEM; XRD*

1. Introduction

High mechanical strength and excellent electrical conductivity of copper matrix composites, among with other properties, ensure a wide application range for these materials. During the last decade, as a consequence of the development of highly reinforced copper alloys, numerous research work was published reporting on diverse processing and forming techniques of these composite materials. Fine ceramic particles, based on metal oxides, nitrides, borides and silicates are most commonly used as composite reinforcements. These ceramic particles can be added to the copper matrix in several different ways such as mechanical alloying [1], internal oxidation [2], combined mechanical alloying and internal oxidation processing [3], and *in-situ* processing [4-11]. However, *in-situ* processing is proved to be one of the most promising composite forming processes. Till now, few techniques of *in-situ* processing have been developed. The most common techniques are a combination of powder grinding in high energy mills and reaction synthesis, spray forming or a chemical reaction in a liquid metal. One version of the latter technique is the atomization of a molten metal or an alloy by an inert gas. Due to the very fast solidification of as-atomized particles, formation of fine inclusions (smaller than 10-15 nm) is easy to achieve. This fact makes this technique superior to the other above mentioned techniques [12].

The main advantage of the *in-situ* process is that the *in-situ* generated reinforcement surfaces tend to remain free of contamination caused by gas absorption or oxidation, and as a

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result, an improved matrix/reinforcement interface bond can be achieved. High mechanical strength, as well as high stiffness and hardness, are the main TiB_2 characteristics. Furthermore, in contrast to most ceramic materials, TiB_2 is electrically and thermally conductive [13]. All previously listed properties suggest TiB_2 as a potential copper reinforcing material in cases where high electrical conductivity of the material is of the prime concern.

In the present work, obtaining of an *in-situ* Cu-TiB_2 composite by powder metallurgy processing using the rapid solidification method (gas atomization) and hot isostatic pressing (HIP) as the consolidation technique, was discussed.

2. Experimental procedure

Prealloys for the atomization process were obtained via vacuum induction melting (VIM). The Cu-Ti and Cu-B alloys with a defined chemical composition were separately melted at 1000°C and afterwards homogenized by casting into a copper mould. The heating and cooling rates during VIM were 100 $Kmin^{-1}$ and 200 $Kmin^{-1}$, respectively. Casting was performed in an argon atmosphere. The prealloy compositions, casting temperatures, casting durations and microhardness of the as-cast materials are listed in Tab. I.

Tab. I. Basic characteristics of the as-cast prealloys used for Cu-Ti-B alloy production

Composition of starting material (wt.%)	*Casting temperature (°C)*	*Casting duration (min)*	*Composition of as cast material (wt. %)*	*Microhardness (HV)*
Cu-4Ti	1100	10	Cu-3.8Ti	190
Cu-1.4B	1100	10	Cu-1.2B	117

The Cu-Ti and Cu-B prealloys were heated from room temperature to 1400°C at 200 $Kmin^{-1}$ rate. The homogenization process lasted 5 min and for that purpose an argon pressure of 3 MPa was applied. The cooling rate of the droplets was in the range of 10^3 to 10^6 Ks^{-1} [14].

Characterization of the atomized powders was performed. It included chemical analysis by means of atomic emission spectrometry, light optical microscopy (LOM) examination, X-ray diffraction (XRD) analysis, sieving and microhardness measurements.

The HIP-ing test tube was made of a thin-sided copper tube, 10 mm in diameter and 200 mm in length. The tube walls were 0.8 mm thick. At 40 mm of the tube length, the tube diameter was reduced to 6 mm. Evacuation of the tube previously heated for 30 min at 580°C was conducted at 100°C for 60 min. When evacuation was completed, the tube was welded using the Cu-Ni electrode with the melting point in the temperature interval between 830°C and 920°C.

HIP-ing was performed at 450°C and 750°C for 10 min in argon protective atmosphere using the "NF" press with the maximal applied pressure of 200 MPa followed by argon quenching to room temperature. All samples were metalographically prepared in the same manner. The sample preparation included grinding with SiC paper, polishing with a diamond suspension and etching in a KLEMM III solution (100 ml distilled water, 11 ml saturated $Na_2S_2O_5$ "stock" solution, 40 g potassium disulfite).

A "Reichert Jung" light optical microscope (LOM) and "Jeol JEM 100C" transmission electron microscope (TEM) were used for the microstructure characterization of the obtained compacts, whereas the compacts density was determined using the standard Archimedes method in xylene. A "Reichert MeF Metallograph" microhardness tester was utilized for obtaining the compacts Vickers microhardness values, applying a 15 g load. A

"Simens D500 PC automatic diffractometer" with CuK_α radiation was used for the XRD analysis.

3. Results and discussion

Since it is well known that the melting temperature of binary copper-based alloys is near 1000°C [15, 16], this temperature was the basic parameter for the preparation of prealloys. Using a copper casting mould, improved homogenization was obtained resulting in randomly distributed alloying elements in a copper matrix (Fig. 1). The presence of coarse equilibrium Cu_4Ti particles in the Cu-Ti (solid solution) matrix is more or less unavoidable due to the low cooling rate during solidification processing.

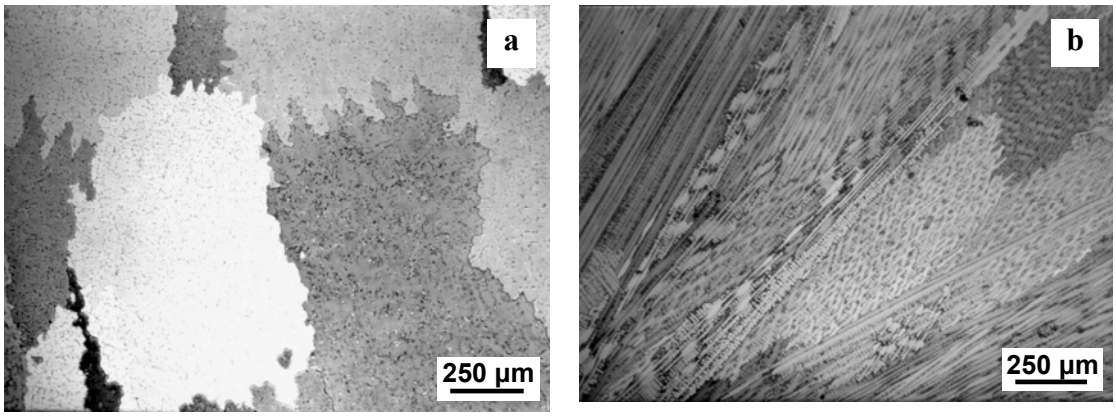

Fig. 1 LOM micrographs showing the microstructure of as cast (a) Cu-3.8Ti (wt.%) and (b) Cu-1.2B (wt.%) prealloy.

Using the produced as-cast material, the Cu-Ti-B alloys were argon atomized at 1400°C. After completing the gas atomization, microstructure characterization of the obtained powder was undertaken. Homogenous distribution of TiB_2 particles in the microstructure could not be observed using LOM (Fig. 3), however it was reflected in the microhardness values (Tab. II).

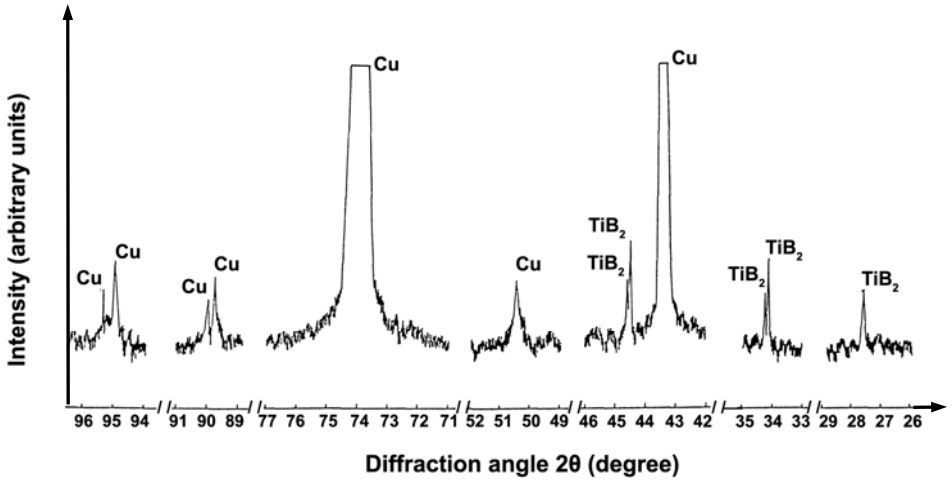

Fig. 2 XRD pattern of the Cu-TiB_2 powder.

Although the XRD analysis of atomized powders showed only the presence of the TiB_2 phase in the copper matrix (Fig. 2), we identified the presence of a certain amount of Ti and a negligible amount of B using additional chemical analysis (see Tab. II).

Diffusivities of titanium and boron in copper were calculated (Fig. 4) using the diffusion coefficients values for titanium and boron in copper at 800°C and 900°C already reported in literature [17], and an extrapolation of literature data. It was shown that convergence of the obtained results with the increase in temperature is the result of lattice expansion. The increase in the diffusion coefficients with increasing temperature points out that small independent concentrations of titanium and boron require longer times for formation of TiB_2 at lower temperatures, whereas the formation of dispersoids is very rapid (*in-situ*) during the atomization process (1400°C).

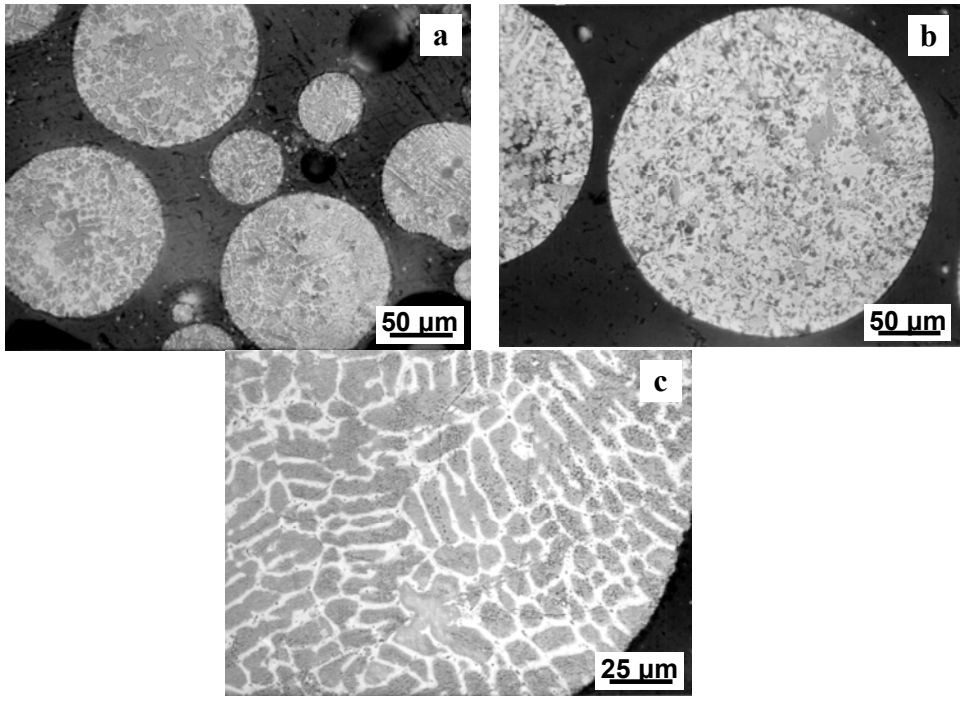

Fig. 3 LOM micrographs showing the microstructure of different as-atomized Cu-0.6Ti-0.02B-2.5TiB_2 (wt.%) alloy powder sieved to fractions: (a) d < 80 µm, (b) 80 µm < d < 150 µm and (c) 200 µm < d < 315 µm.

A homogenous distribution of very hard TiB_2 particles in the primary matrix should explain the significant resistance to deformation in the as-atomized powders (Tab. II).

Tab. II. Characteristics of Cu-Ti-B atomized powders.

Composition of as cast materials	*Chemical analysis of as atomized material (wt.%)*			*Microhardness (HV)*		
(wt.%)	*Ti*	*B*	TiB_2	$d^*<80\mu m$	$80\mu m<d^*<150\mu m$	$200\mu m<d^*<315\mu m$
Cu-3.8Ti Cu-1.2B	0.6	0.02	2.5	230	227	229

* powder particle diameter

The alloy particles are spherical in shape with a homogenous structure and characteristic dendrite morphology. The TiB_2 dispersoids are uniformly distributed preferentially within the interdendritic spaces through the entire particle. The microhardness of the as-atomized powders as a function of the powder particle size is presented in Tab. II, revealing the surprising fact that the powder particle size decrease does not affect the microhardness values. The conclusion that can be drawn from the present results is that distribution of the dispersoids in the powder structure has a much greater influence on the powder particle microhardness than the particle size itself. This was the main reason why the HIP-ing procedure was chosen as the powder compacting method in this study.

It is well known that compaction of spherical particles of different sizes results in lower compact porosities. Namely, during the compacting treatment smaller powder particles will fill in the empty spaces between larger neighboring spherical particles [18]. In this way the powder apparent density can reach even 60 % of the theoretical material density facilitating easier powder compaction. For compaction, the powder mixture that consisted of spherical particles of different sizes was used without any concern that this can bring about the variation in the compact microhardness (results presented in Tab. II clearly show that the microhardness values are practically identical for different powder fractions).

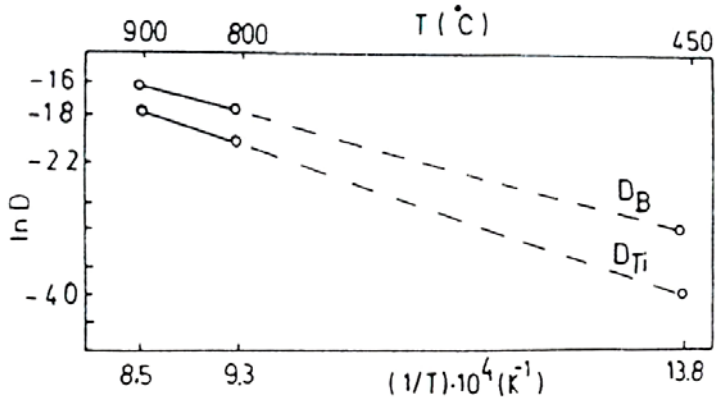

Fig. 4 Calculated diffusion coefficients for titanium and boron in copper.

In order to fully densify the copper composite powder using the HIP process, it was necessary, in addition to finding optimal parameters for hot isostatic pressing, to conduct certain preceding actions regarding the choice, manufacturing and evacuation of the test tube. Uniform impact force distribution on the powder particles was provided using a thin-sided test tube, in which the thickness of the walls did not exceed 1 mm. Reduction of the test tube cross section was used in order to avoid contact between the test tube and the powder particles during welding, as well as to achieve higher safety level during the test tube preparation procedure. After evacuation and welding, welding quality control was carried out. Afterwards, the test tube was tested in an aggressive environment for 48 h and it was concluded that the deposited Cu-Ni layer was not damaged, Fig. 5. After the quality control examination was completed, the test tubes were filled with Cu-TiB_2 composite powders.

Fig. 5 X-ray recording of the thin-sided test tube.

An investigation of Cu-Ti-B composites produced by gas atomization and HIP-ing was challenging because of little literature data available. The main concern was compacting composites with fine and hard dispersoid particles to near theoretical density without changing the rapidly solidified microstructure.

Tab. III. HIP-ing parameters and properties of the obtained Cu-TiB_2 composite.

Composition of as HIP-ed materials (wt.%)	*Temperature (^oC)*	*Time (min)*	*Pressure (MPa)*	*Density (g/cm^{-3})*	*Open porosity (%)*	*Microhardness (HV)*
Cu-0.6Ti-0.02B-2.5TiB_2	750	10	200	8.43	0.05	210

Nearly nonporous compacts were produced (see Fig. 6 and Tab. III) by HIP-ing for 10 min at 750^{o}C and applied argon pressure of 200 MPa. After HIP-ing, the compacts were rapidly quenched to room temperature.

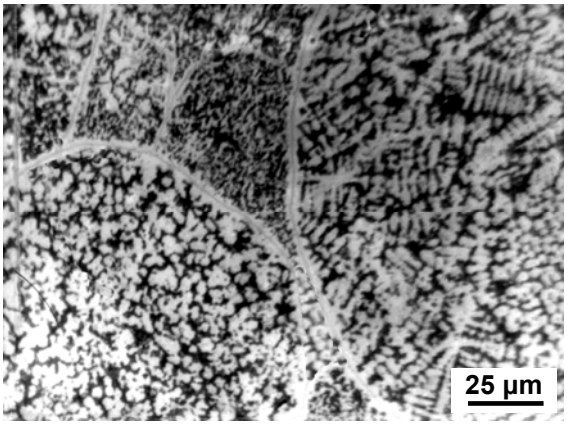

Fig. 6 LOM micrograph showing the microstructure of the HIP-ed Cu-TiB_2 composite compact.

During HIP, densification occurs as a result of powder particle deformation near the surface of their contacts, power law creep and diffusion. The overall behavior of materials under the influence of applied pressure and high temperature is very complex because all of the above mentioned densification mechanisms depending on the particle size, processing parameters and other material properties in a different way.

From Fig. 5 and the data presented in Tab. III one can conclude that parameters selected for the HIP-ing process provided sufficient atomic mobility, which is necessary for the high pressure sintering completion and elimination of porosity. At 750^{o}C the material deformation induced by thermally activated dislocation movements is possible, and therefore time dependent densification mechanisms (first of all, power law creep and diffusion) were significant in relation to the overall densification rate. It can also be noticed (Fig. 6 and Tab. III) that microstructure degradation and microhardness changes of the produced compacts did not occur.

The HIP-ing temperature could be lower if copper oxides at the primary particle boundaries were removed. Although the applied pressure was relatively high (200 MPa), primary particle boundaries (PPB) were visible in the microstructure, Fig. 5. The presence of these boundaries in the microstructure after densification is characteristic of this compacting technique.

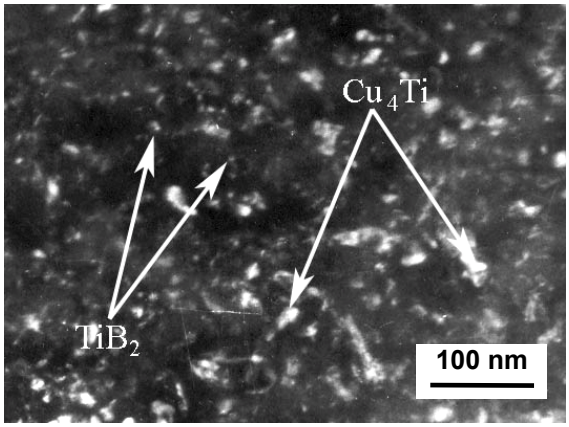

Fig. 7 TEM micrograph showing the dispersoid TiB_2 particles and Cu_4Ti equilibrium precipitates present in the copper matrix.

In contrast to the rapidly solidified powders that contained only TiB_2 dispersoids, in the microstructure of HIP-ed compacts, coarse particles of Cu_4Ti precipitates can also be distinguished. This microstructure is a consequence of lower cooling rates after sintering, compared to cooling rates after atomization. The presence of Cu_4Ti precipitates causes a small decrease of microhardness values, Tab. III. A uniform distribution of the *in-situ* formed TiB_2 dispersoids in the metal matrix can be observed in the TEM micrograph of the produced compacts, Fig. 7. This distribution of the dispersoids was achieved during the atomization processing and was retained during the HIP-ing.

4. Conclusion

The following conclusions can be drawn from the present study:

1. Homogenous distribution of the alloying elements in the Cu-Ti-B prealloy during atomization is highly dependent on the correct choice of titanium and boron amounts, as well as on appropriate melting parameters.
2. Successful preparation of the *in-situ* formed TiB_2 dispersoids in the copper matrix powders was performed via argon atomization at 1400^{o}C.
3. The rapidly solidified Cu-TiB_2 powders are characterized by a homogenous microstructure and the presence of finely dispersed TiB_2, a certain amount of Ti and a negligible B content.
4. The presence of finely dispersed TiB_2 particles is the main reason for the high microhardness values of the Cu-Ti-B powders.
5. Nonporous compacts with a homogenous microstructure and high microhardness values were obtained during 10 min of HIP-ing at 750^{o}C under applied argon pressure of 200 MPa. A uniform distribution of the TiB_2 particles in the copper matrix was achieved in the rapidly solidified powders and was not altered after the HIP-ing process.

Acknowledgements

The results presented in this paper were realized with financial support of the Ministry of Science and Technological Development of the Republic of Serbia through project No. 142027.

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Садржај: *Правилним избором количине легирајућих елемената, као и избором најповољнијег поступка топљења, израђене су предлегуре Cu-Ti і Cu-B. Топљењем, предгревањем и распршивањем растопа предлегура помоћу аргона добијен је прах Cu-TiB_2 композита. Брзо очврснути прах је консолидован топлим изостатичким пресовањем, HIP-ом (hot isostatic pressing). С обзиром да је познато да се са смањењем величине честица ојачавајуће фазе може утицати на повећање тврдоће композита, основни циљ истраживања, презентованих овим радом, је био добијање што ситнијих честица дисперговане фазе коришћењем стандардних техника металургије праха. Извршено је испитивање микроструктуре и микротврдоће предлегура, атомизираних прахова и компаката добијених HIP-ом. Резултати испитивања показали су да су честице TiB_2, формиране in-situ у процесу атомизације, биле величине ~10 nm и да су се одликовале хомогеном расподелом у бакарној основи. Присуство TiB_2 нано-честица у основи бакра довело је до значајног пораста микротврдоће код Cu-TiB_2 композита.*

Кључне речи: *Cu-TiB_2 композит, металургија праха, топло изостатичко пресовање, TEM, XRD*